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(54) **Solar concentrator plates/ a luminescent solar collector comprising such plates/ a method of converting solar energy to electrical energy using such plates and the use of certain dyes insuch plates.**

(57) The invention provides a solar concentrator plate doped with a dye selected from the group consisting of Orange-Red, Fluorol, oxazine-4-perchlorate, LDS 730, LDS 750, BASF 241, BASF 339 and combinations thereof with each other and with Clear or 3-phenyl-fluoranthene. The plates can be used in a luminescent solar collector for use in converting solar to electrical energy.

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SOLAR CONCENTRATOR PLATES, A LUMINESCENT SOLAR COLLECTOR COMPRISING SUCH PLATES, A METHOD OF CONVERTING SOLAR ENERGY TO ELECTRICAL ENERGY USING SUCH PLATES AND THE USE OF CERTAIN DYES IN SUCH PLATES

The present invention relates to solar concentrator plates. More particularly, the present invention relates to solar concentrator plates having high efficiency and stability and to luminescent solar concentrators containing such plates.

As is known, the use of solar energy as a power source is not yet cost competitive with other power generating methods because of the high cost of solar cells and tracking solar energy concentrators. In an attempt to lower cost by reducing the cell area during the last years much work has been based on the concept of a luminescent solar concentrator which can absorb solar light from a large insolated area and concentrate the emitted fluorescent light to a small area to which photovoltaic cells can be attached. Luminescent solar concentrators (LSC) are based on the entrance of solar radiation into a homogeneous medium collector containing a fluorescent species in which the emission bands have little or no overlap with the absorption bands. This emission is trapped by total internal reflection and concentrated at the edge of the collector by the geometrical shape which is usually a thin plate. Thus the concentration of light trapped in the plate is proportional to the ratio of the surface area to the edges. The advantages of LSC over conventional solar concentrators are the following:

a) High collection efficiency of solar light direct and diffuse;

b) Good heat dissipation from the large area of the collector plate in contact with air, so that essentially "cold light" is used for convertor devices such as silicon cells, whose efficiency is reduced by high temperatures;

c) tracking of the sun is unnecessary; and

d) Choice of the luminescent species allows optimal spectral matching of the concentrated light to the maximum sensitivity of the photovoltaic process, minimizing undesirable side reactions in the PV cells.

Two types of homogeneous media have been proposed so far as substrates for the fluorescent species, glass [see, e.g., Israel Patent 56,742 corres. to U.S. Patent, 4,367,367 and U.K. Patent 2,028,859; R. Reisfeld and S. Neuman, Planar solar energy convertor and concentrator based on uranyl doped glass, Nature 274 (1978) 144; R. Reisfeld and T. Kalisky, Improved planar solar convertor based on uranyl neodymium and holmium glasses, Nature 283 (1980) 281; R. Reisfeld and C.K. Jorgensen, Luminescent solar concentrators for energy conversion, Structure and Bonding 49 (1982) 1; A. Kisilev and R. Reisfeld, Spectral characteristics and fluorescence quantum efficiencies of Cr (III) in phosphate and silicate glasses with Li and Be modifiers, Solar Energy (1984); R. Reisfeld, E. Greenberg, A. Kisilev and Y. Kalisky, Collection and conversion of solar energy for photo-converting systems, Third Int'l. Photochem. Conversion and Storage of Solar Energy, Colorado, Aug. 1980, Photochem. Conv. and Storage of Solar Energy, Ed. J.S. Connolly, Academic Press (1981) 364, and A. Kisilev, R. Reisfeld and H. Tzehoval, Manganese and chromium doped phosphate and silicate glass for fluorescent concentrators, Fourth Int'l. Conf. Photochem. Conversion and Storage of Solar Energy, Jerusalem, Aug. 1982, Book of Abstracts, p. 299],and organic plastic materials in which the fluorescent species are incorporated into the bulk of the host [see, e.g., J.S. Batchelder, A. H. Zewail and T. Cole, Appl. Opt. 18 (1979) 3090; A. Goetzberger and V. Wittwer, Solar Cells, 4 (1981) 3, and J.M. Drake, M.L. Lesiecki, J. Sansregret and W.R.L. Thomas, Appl. Opt. 21 (1982) 2945.]

Recently published articles have also proposed a concept of light concentration in which a thin film of dye is deposited on a glass [see, e.g., P.S. Friedman, Opt. Eng. 20 (1981) 887; C.F. Rapp and N.L. Boling, Proc. 13th IEEE Photovoltaics Specialists and R. Reisfeld and C.K. Jorgensen, Structure and Bonding 49 (1982) p. 32].

In such a configuration a fluorescent dye dispersed in PMMA or in a related transparent polymer is brought into optical contact with the glass. Fluorescence emitted from the dye is trapped in the combined system and emitted in a concentrated form from the edges. In order that the trapping be efficient in the composite configuration the refractive index of the film should be either slightly less or the same as that of the substrate.

In addition, quite recently, porous fluorescent materials have been suggested for LSC by R. Reisfeld, N. Manor and D. Avnir, Solar Energy Materials, 8 (1983) 399.

In recent years many articles and patents have dealt with solar concentrators including the article by W.H. Weber and John Lambe in Applied Optics, Vol. 15, No. 10, pp. 2299-2230, Oct. 1976, the article by A. Goetzberger and W. Greubel, Applied Phy. 14, 123-139 (1977) and U.S. Patents 4,110,123; 4,140,544; 4,144,097; 4,159,212; 4,173,495; 4,188,238 and 4,367,367.

As is known, the performance of LSC is given by the effective concentration ratio which is the product of the geometrical factor and the optical conversion efficiency of the collector. The geometrical factor is the ratio of the surface Area A_s to the area of the plate edges A_ℓ. The optical conversion efficiency n_{opt} of the collector plate may be defined as the ratio of light delivered from the total edges to the light incident on the collector plate.

$$n_{opt} = P_{out}/P_{in} \qquad (1)$$

where P_{in} is the total solar power in watts incident on the collector and P_{out} is the power delivered from the total edges.

The optical conversion plate efficiency depends on the following factors:

1. The fraction of the light absorbed η_{abs};
2. Quantum efficiency of the fluorescent species η_{ℓ};
3. Stokes efficiency which is the ratio between the average energy of emitted photons to the average energy of adsorbed photons

   η_s, $\eta_s = \nu_{emis}/\nu_{abs}$;
4. The fraction of the light trapped in the collector η_t;
5. Transport efficiency η_{tr}, taking into account transport losses due to matrix absorption and scattering; and
6. Parasitic efficiency η_{sel}, taking into account parasitic losses due to self-absorption of the colorants.

Factors 4 and 5 depend on the host material of the collector. Factors 1, 2, 3 and 6 depend on the nature of the absorbing and fluorescent species such as the transition probability for absorption, width of the spectral bands, energy transfer efficiencies from the donor to the acceptor molecules and non-radiative transfer probabilities of the fluorescent species.

The first four parameters were studied and determined for purposes of the present invention for inorganic glasses doped with fluorescent ions and for thin films of dyes deposited on glasses and plastics.

The expression for the optical efficiency including reflection is given by

$$\eta_{opt} = (1 - R)\eta_{abs}\eta_{\ell}\eta_{s}\eta_{t}\eta_{tr}\eta_{se\ell} \qquad (2)$$

where $n_t = 1 - \sqrt{1/n^2}$ (n = refractive index), n_{sel} includes losses due to absorption of luminescent light by the colorant, n_{tr} scattering losses due to glass imperfections and R = Fresnel reflection coefficient (approx. = 4%).

The current gain G_i is the ratio of the electrical current delivered from the PV cell complex to the edge of the LSC relative to the current obtained from the identical cell when both are turned perpendicular to the solar radiation. Since the current is proportioned to the energy output its gain is important in the economical evaluation of a collector.

In these studies it was noted that the self-absorption is low in the inorganic material especially when the absorption and emission arises from different electronic levels in the same ion or the absorption and emission originate from different species which transfer energy between them. It may be quite appreciable in organic dyes which have overlapping absorption and emission spectra when the dyes are homogeneously dispersed in a plastic or liquid solvent. This may decrease significantly the optical plate efficiency of the collector based on organic dyestuffs in homogeneous media. The self-absorption is reduced in the thin-film configuration where the emitted luminescence travels in an optically transparent medium. Self-absorption can also be diminished to some extent by utilizing energy transfer from an acceptor molecule to the donor molecule thus separating the absorption and emission bands.

As can be seen from the above-mentioned patents and publications, so far mostly laser dyes have been used as fluorescent molecules in LSC. These molecules have usually good quantum efficiencies, however their disadvantages is their photo-instability.

Since the photo-stability of dyes for LSC is of vital importance for the long range performance of LSC it is an object of the present invention to provide solar concentrator plates and LSC based thereon having much greater stability than those previously suggested in the prior art.

It has now been found, however, that dyes such as Coumarin 153®, Coumarin 311®, Rhodamine 6G® and Sulfarhodamine B® described in the prior art as being preferred for the presently proposed uses in fact are bleached in sunlight within 2-3 days and thus do not possess the necessary photostability for use in solar concentrator plates and LSC.

Similarly, of the hundreds of dyes available on the market most of those tested exhibited similar lack of photostability.

Thus it was surprising to find that Horn Radglo fluorescent pigments GF Orange-Red® and GF Clear® of Ciba-Geigy-Tan-Horn-Pigment Chemie N.V. Holland, Fluorol 555®, LDS 730® and LDS 750® of Exciton Chemical Co. INc., Dayton, Ohio, laser grade Oxazine-4-perchlorate of Kodak and BASF 241, BASF 339 and 3-Phenyl Fluoranthene all possess both the necessary photostability and concentrator plate efficiency which have long been sought and heretofore not exhibited by most dyes.

Thus, e.g., plates covered with Orange-Red, Clear, Fluorol and Oxazine-4-perchlorate have been placed in indirect and direct sunlight passing through a glass for periods in excess of two years without any appreciable changes in absorption and emission characteristics, and the remaining dyes according to the present invention also possess superior stability characteristics when compared with the above-mentioned prior art dyes.

It has also now been found that the photo-stability of the dye in the thin film configuration is greatly enhanced when the dye is covered by a thin film of inorganic glass doped by cerium (III), or alternatively, if the organic dye is added to the glass-forming mixture which is then deposited as a thin film on a PMMA substrate.

Thus according to the present invention there is now provided a solar concentrator plate doped with a dye selected from the group consisting of Orange-Red, Fluorol^{555}, Oxazino-4 perchlorate, LDS 730, LDS 750, BASF 241, BASF 339 and combinations thereof with each other and with Clear or 3-phenyl-fluoranthene.

Similarly, the present invention is directed to all dyes having different commercial names but nevertheless having the same dye pigment identifiable by the data set forth in Table II hereinafter.

The present invention also provides a luminescent solar collector for high efficiency conversion of solar energy to electrical energy wherein solar energy is converted to fluorescent radiation at longer wave lengths at which photovoltaic cells have a better efficiency comprising a solar concentrator plate according to the present invention said plate being provided with a photovoltaic cell at at least one of its lateral edges, said photovoltaic cell having a high efficiency in the region of the spectrum of the respective fluorescent radiation.

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In the preferred embodiments of the present invention the dye or combination of dyes is dispensed in a thin film of glass or plastic material covering said plate, however other embodiments wherein said dye is incorporated in a plastic or glass plate are also included herein.

The dye film can then be covered by a glass film including cerium (III), or without cerium (III), which is polymerized on the plate.

Especially preferred embodiments are those wherein said plate is doped:

a) with BASF 241 + BASF 339 + Clear

b) with BASF 241 + BASF 339

c) with BASF 339 + Clear

d) with a combination of Orange-Red and Clear dyes;

e) with a combination of Orange-Red and Fluorol dyes;

f) with a combination of Orange-Red and oxazine-4-perchlorate dye;

g) with a combination of Orange-Red and LDS 730;

h) with a combination of Orange-Red and LDS 750; or

i) with one of Orange-Red, Fluorol, or LDS-730 dyes alone.

The invention will now be described in connection with certain preferred embodiments with reference to the following illustrative figures and examples so that it may be more fully understood.

It will be understood however that it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

EXAMPLES

General Procedure

For preliminary investigations the dyes were dissolved in chloroform or 1,2-dichlorethane, analytical grade. For coating glass or plastic substances with the chosen dyes, a solution of PMMA (Matheson, Coleman & Bell) in dichloroethane was prepared. The optimal PMMA concentration of 100 gm/l was determined by repeated experimentation with glass substrates. The dyes were dissolved in this stock solution.

Glass microscope slides 25 mm x 75 mm x 1 mm and PMMA plates 10 x 10 cm x 0.3 cm were used as substrates. These were heated to 42 $\pm$ 2°C prior to dipping in the dye solution at the same temperature, and then dried for 3 hours. Precautions were taken to eliminate interferring substances throughout the process.

The coloured slides were dipped in a solution having the following materials:

10 ml tetramethylorthosilicate (tetramethoxysilan)

10 ml boric acid (5.5 gm in 100 ml alcohol)

5 ml aluminum ethoxide in dichloroethane

5 ml potassium ethoxide in dichloroethane

1 ml 1% ethanol solution of cerium chloride

5 ml methylamine (33% CH_3NH_2 in ethanol)

1.3 ml polyethylene glycol-400-monooleate (emulsifier)

made up to 100 ml with dichloroethane.

The temperature of this solution and environment was 40°C. After dipping, the thin layer of tetramethoxysilan was transformed by polymerization into a glass film covering the coloured slide.

Similar coating techniques can be also found in H. Dislich, J. Noncrystalline Solids 57 (1983) 371 and H. Dislich and E. Hussma Thin Solid Filsm 77 (1981) 129.

In order to achieve as uniform films as possible, an arrangement for coating the substrates was set up which consists of a glass container for holding the PMMA-dye solution, a motor driven spindle and a wire windable and unwindable around said spindel. Said wire passes over a pulley wheel positioned over said container and is inserted through holes provided at one edge of the plate to be immersed. The time of dipping is then uniformly controlled by said velocity of the motor immersing and pulling out said plates.

For coating substrates with the chosen dyes, a solution of PMMA (Matheson, Coleman and Bell) in dichloroethane was prepared. The optimal PMMA concentration of 100 gm/ℓ was determined by repeated experimentation. The dyes were dissolved in this stock solution. The optimal concentrations of the chosen dyes were:

Clear	(Ciba - Geigy - Ten - Horn textile dye)	200 g/ℓ
Orange-Red	(Ciba - Geigy - Ten - Horn textile dye)	20 g/ℓ
Fluorol 555	(Exciton laser grade dye)	0.65 g/ℓ
LDS 730	(Exciton laser grade dye)	0.2g/ℓ
LDS 750	(Exciton laser grade dye)	0.2g/ℓ
BASF 241		5.0g/ℓ
BASF 339		2.0g/ℓ
3-Phenyl Fluoranthene		5.0g/ℓ

Absorption spectra were taken on a Cary-14 spectrophotometer using identical substrate glasses as blanks. Emission and excitation spectra were measured at room temperature on a spectrofluorimeter using a 500 W Xenon dc source, two Bausch & Lomb monochromators and an EMI 9558 photomultiplier connected through a Vibron amplifier to a Kipp and Zonen strip chart recorder. Sample excitation was through the plate face and the spectra presented here were obtained from the plate edge approximately 10 mm away from the excitation area.

The fraction of solar light absorbed (n_{abs}) was measured using a broad band radiometer (Ophir Optics). The measured transmission of each sample was divided by the measured transmission of a glass blank. Thus the result is corrected for surface reflection losses. The experimental error is ± 5%.

Refractive indices of the dye lasers were measured by the Brewster angle method and with the sodium D-line. The experimental error is less than ± 1%. Table I gives the measured refractive indices and calculated fraction of light trapped for Orange-Red, Clear and a combination of Orange-Red and Clear.

EXAMPLES 1 - 3

TABLE I

MEASURED REFRACTIVE INDICES AND CALCULATED TRAPPING EFFICIENCIES

Dye	Refractive Index n	Trapping Efficiency n_t	Optical Density at Peak Maximum
OR	1.507	0.75	0.99
Cl	1.595	0.78	1.00
OR + Cl	1.591	0.78	1.00

OR = Orange Red   Cl = Clear

Example 4

In order to increase the solar absorption, LSC plates coated by more than one dye were constructed in a multilayered film LSC. The order of coating dyes was chosen such that the shortest wavelength absorbing dye was followed by the next shortest wavelength dye and the outside layer contained the longest wavelength dye: e.g., Clear-Fluorol-Orange/Red. Finally the plate was covered by a thin film of glass containing 0.1% Ce^{3+} forming a plate with the following sequential layers.

glass + Ce^{3+}, orange-red, fluorol-555, clear, undoped substrate, clear, fluorol-555, orange-red, glass + Ce^{3+}.

Example 5

The polymer or glass plate was coated on one side with BASF 241 and on top of this another layer containing BASF 339 was deposited. This was finally covered with glass containing Ce^{3+} by the deposition of tetramethoxysilane containing Ce^{3+}. On the second side Clear was deposited and covered by Ce^{3+}-containing glass layer.

Quantum efficiency was calculated using the comparison with standard material method (as reported in Israel J. Chem. 7 (1969) 613, R. Reisfeld, J. Res. Nat. Bur. Standards, 76A (1972) 613).

The following equation was used:-

$$\eta_u = \eta_s \frac{F_u \cdot A_s \cdot I_{\lambda_{sEX}}}{F_s \cdot A_u \cdot I_{\lambda_{uEX}}} \cdot \frac{n_u^2}{n_s^2}$$

where η_u and η_s are quantum yields of the unknown and standard respectively, n_u and n_s are indices of refraction, A the absorbance at the wavelength of excitation, F the integrated area under the emission spectrum and $I_{\lambda_{Ex}}$ is the relative irradiance of the light at wavelength of excitation.

Eu (III) in germanate glass excited at 453 nm was used as a standard. Quantum yield of Eu (III) at 458 nm excitation is equal to 0.75(12). Refractive index of germanate glass was taken as n_D = 1.64. (Refraction indices of phosphate and silicate glasses are 1.51).

For LSC evaluation the samples were placed on an apparatus constructed for this purpose which enables alignment of the glass and reference cell relative to the sun. OCLI photovoltaic cells of dimensions 20 mm x 4 mm with antireflective coating were apertured down to expose a 1 mm strip. Alternatively silicon amorphous cells provided by Dr. G. A. Swartz of RCA were used. One cell was used as reference with its plane parallel to the glass face. Another identical cell was placed in optical contact with the glass edge using parafin oil for index matching. The short circuit current was measured with a Tabor Electronics digital multimeter 6088. Care was taken to shade the measuring

cell from direct sunlight so that cell current without sample was less than 4% of reference current.

The attached figures present the absorption spectra of the dyes on glass in which:

Figure 1 presents absorption spectra of oxazine-4 alone, concentration 2×10^{-4} mole/l; Orange Red alone, concentration 20 gm/l; and Orange Red 20 gm/l, coated over oxazine-4,0.01 gm/l.

Figure 2 presents the absorption spectra of Clear alone, concentration 200 gm/l; Orange Red alone, concentration 20 mg/l; and Orange Red, 20 gm/l, coated over Clear, 200 gm/l.

Figure 3 shows the emission spectrum of Orange Red (excitation at 530 nm); of oxazine-4 (excitation at 610 nm); and of Clear (excitation at 375 nm).

Figure 4 gives the excitation spectrum (a) of Orange Red coated on Clear (emission at 620 nm) and emission spectrum (b) of Orange Red coated over Clear (excitation at 530 nm); the excitation spectrum (c) of Orange Red coated over oxazine-4 (emission at 665 nm) and emission spectrum (d) of Orange Red coated over oxazine-4 (excitation at 530 nm).

Figure 5 gives the absorption and emission spectrum of LDS 750 and LDS 730.

Figure 6 presents the absorption and emission spectra of PMMA coated by fluorol.

Figure 7 presents the absorption spectra of PMMA coated by Clear, Fluorol and Orange Red as in Example 1.

Figure 8 presents the emission spectra of PMMA coated by Clear, Fluorol and Orange Red as in Example 1.

Figure 9 presents the absorption spectrum of PNMA coated by Clear, BASF 241 and BASF 339. Figure 10 presents the emission spectrum of PMMA coated by Clear, BASF 241 and BASF 339.

All concentrations in the figures are in starting solution, PMMA concentration 100 gm/l in dichloroethane. The dye optimum concentrations were chosen as those having maximum quantum efficiency.

It should be noted that the sensitivities corresponding to the curves in each of the figures vary by factors of up to 10, thus Clear has the highest, and oxazine-4 the lowest emission intensity in the figures.

Optical efficiencies of sample plates as set forth in the tables hereinafter were measured outdoors and behind a glass window using an adjustable positioning table specially constructed to enable alignment of a sample and reference cell relative to the sun and dimensions of the samples. Single crystal silicon photovoltaic cells were used. One cell was used as reference with its plane parallel to the sample face. Another identical cell was placed in optical contact to the sample edge using paraffin oil for index matching. The short circuit current was measured with a Tabor Electronics digital multimeter 6088.

Referring now to Table II there is provided the characterizing absorption and emission maxima quantum efficiency and Stokes shift for various dyes used in the present invention when coated on glass or on polymeric transparent material such as PMMA.

TABLE II

ABSORPTION AND EMISSION MAXIMA, QUANTUM EFFICIENCY AND STOKES SHIFT FOR VARIOUS COATED GLASSES

Dye		Peak Absorption λ_{max}nm	Peak Emission λ_{fl}nm	η %[1]	Stokes Shift cm^{-1}
OR	Thin film on glass	530	620	78.5	2736
Cl	"	375	440	~90.0	3939
Fl	"	440	495	88.0	2525
LDS-730	"	620	700	~30.0	1844
LDS-750	"	550	685	~20.0	3583
OX	"	610	655	36.6	1126
OX	in methanol[14]	609	646	63.0	941
OX	in ethanol[14]	614	651	62.0	926

OR = Orange Red Cl= Clear OX = Oxazine-4

Fl = Fluorol 3-Ph.F = 3-Phenyl Fluoranthene

Table III presents the LSC performance characteristics of several efficiency of the coated plates η_{opt} $G_i = I_{edge}/I_{reference}$, G = geometric factor which is 0.94 therefore $\eta_{opt} = G_i/G$.

The symbols in this table are as follows, dye symbol - glass means that dye was deposited on one side of glass, dye symbol - glass - dye symbol means dye was deposited on both glass sides. The dye at the left of the glass means that the covered side was exposed to the sun and the glass at left means that the glass side was exposed to the sun.

If two dyes are present the order of coverage is as in the text, for example OR - OX -Gl - OX - OR means that the glass

was covered on both sides, first by OX and then by OR.

As can be seen from Table III the best plate efficiency of 14% is obtained when Orange Red covers a glass coated first by Clear. This arises from the fact that the escaping light from Clear is absorbed by Orange Red. The strong fluorescence of Clear having quantum efficiency of about 90% (Table III) is trapped in the Orange Red. Here we have a case of energy transfer which may be of the radiative or nonradiative type between Clear and Orange Red which is a result of the overlap of the Absorption spectrum of Orange Red and the emission spectrum of Clear.

The emission of Orange Red overlaps the maximum sensitivity of gallium arsenide solar cells which have about 60% efficiency at these wavelengths thus one can expect a collector efficiency of 7.2% for a plate coated by Clear and Orange Red and coupled to a gallium arsenide cell.

Even better efficiencies are obtained of about 35% when a combination of Orange Red and Clear or Orange Red and Fluorol cover a PMMA plate.

Discussion

The best efficiencies were obtained with the combination BASF 241, BASF 339 and Clear. The values of optical efficiencies obtained when the plates were coupled to silicon cells or gallium arsenide cells are presented in Table IV. The best efficiency of 0.43 towards direct light was obtained with a combination of BASF 241, BASF 339 and Clear coupled to GaAs cells.

TABLE III

PERFORMANCE CHARACTERISTICS OF THE PLATES

Dye	G_1	η_{opt}
C1- G1	0.187	0.020
G1-C1	0.173	0.018
C1-G1-C1	0.276	0.029
OR-G1	0.550	0.056
G1-OR	0.530	0.056
OR-G1-OR	0.720	0.077
OX-G1	0.131	0.014
G1-OX	0.133	0.014
OX-G1-OX	0.128	0.014
OR-OX-G1	0.182	0.019
G1-OX-OR	0.199	0.021
OR-OX-G1-OX-OR	0.175	0.019
OX-OR-G1	0.157	0.017
G1-OR-OX	0.177	0.019
OX-OR-G1-OR-OX	0.147	0.016
OR-C1-G1	0.458	0.049
G1-C1-OR	0.480	0.051
OR-C1-G1-C1-OR	1.000	0.126

TABLE III

PERFORMANCE CHARACTERISTICS OF THE PLATES

(cont.)

Dye	G_i	η_{opt}	
Cl-OR-Gl	0.642	0.068	*
Gl-OR-Cl	0.634	0.067	
Cl-OR-Gl-OR-Cl	0.789	0.054	
Cl-OR-Gl	0.730	0.077	**
Gl-OR-Cl	0.900	0.096	
Cl-OR-Gl-OR-Cl	0.970	0.103	
OR-Cl-Gl-Cl-OR	1.090	0.140	
OR-Cl-P-Cl-OR	1.77	0.354	*
OR-Fl-P-Fl-OR	1.80	0.360	

G_i = current gain = $I_{edge}/I_{reference}$ = I_s/I_r

G = geometrical factor = $\dfrac{\text{surface area of glass}}{\text{edge area}}$ = 9.4

G = geometrical factor = $\dfrac{\text{surface area of PMMA}}{\text{edge area}}$ = 5

Gl = glass   P = PMMA plate (10 cm x 10 cm x 0.5 cm)

*silicon cell 20 mm x 1 mm

** amorphous silicon cell 6 mm x 8 mm

TABLE IV - EXPERIMENTAL PLATE EFFICIENCIES η_{opt} WITH DIRECT RADIATION:

PMMA PLATE HAVING DIMENSIONS 10 x 10 x 0.3 cm WITH AND WITHOUT DYE FILM.

PMMA Plate	Dye Film(s)	Silicon Cell		Gallium Arsenide Cell	
		Gi = Is/Ir	η_{opt} = Gi/GF	Gi = Is/Ir	η_{opt} = Gi/GF
With dye in bulk GS 2152		1.57	0.19	2.93	0.35
With dye in bulk GS 2152	Clear	1.75	0.21	3.43	0.41
Undoped	BASF 339	1.60	0.19	3.20	0.40
"	BASF 339 + Clear	1.75	0.21	2.62	0.32
"	BASF 241	1.70	0.20	2.98	0.36
"	BASF 241 + BASF 339	1.65	0.20	3.40	0.41
"	BASF 241 + BASF 339 + Clear	1.73	0.21	3.56	0.43
"	BASF 241 + BASF 339 + 3 Phenyl Fluoranthene	1.78	0.22	3.6	0.42

GF = 8.3

Tables IV and V give examples of calculated and experimentally found plate efficiencies of some of the solar concentrator plates of dimensions given in Table III.

Tables VI and VII present the results obtained for PMMA plates covered by thin films of Clear and Orange-Red dyes. Two different experiments were conducted on these plates:

a. Covered plates 10 cm by 10 cm and various thickness (Table VI).

b. Covered plates with thickness of 0.86 cm and different areas (Table VII).

CALCULATED AND EXPERIMENTAL PLATE EFFICIENCIES FOR THIN FILM LSC

Dye	λ_{abs} nm	λ_{fl} nm	η_{abs}	η_{l}	η_{s}	η_{t}	η_{opt} calc.	G_i exp.
OR	530	620	0.27	0.79	0.85	0.75	0.117	0.077
Cl	375	440	0.15	0.90	0.84	0.78	0.076	0.029
OR + Cl			0.42	0.6	0.85	0.78	0.144	0.140
OX	610	655	0.10	0.37	0.93	0.75	0.022	0.014
LDS-730	620	700	0.20	0.30	0.89	0.75	0.035	
LDS-750	550	685	0.10	0.20	0.80	0.75	0.010	
BASF 241	525	650	0.39	1.00	0.81	0.75	0.20	0.20
BASF 339	580	660	0.39	0.95	0.88	0.75	0.21	0.19

$\eta_{opt} = (1 - R)\eta_{abs}\eta_{l}\ \eta_{s}\ \eta_{t}\ \eta_{tr}\ \eta_{sel}$

$(1 - R) = 0.96$

$\eta_{tr} \cdot \eta_{sel} = 0.90$

TABLE VI PMMA Plates Covered with Clear + Orange-Red.

Size 10 × 10 cm and Different Thickness

d (cm)	GF	$G_1 = \frac{I\ sample}{I\ ref.}$	$\eta_{opt} = \frac{G_1}{GF}$
0.17	14.7	1.14	0.08
0.24	10.4	1.25	0.12
0.28	8.9	1.31	0.15
0.32	7.8	1.37	0.18
0.475	5.3	1.17	0.22
0.86	2.9	0.78	0.27
1.04	2.4	0.80	0.33
1.68	1.49	0.60	0.40

I sample - current measured from cell attached to the LSG plate, using index matching liquid

I ref. - current measured from cell directed to sun

GF - geometric factor $GF = \frac{\ell^2}{4\ell d}$

ℓ - edge length

d - thickness

TABLE VII PMMA Plates Covered with Clear + Orange-Red Thickness of 0.86 cm and various size

ℓ (cm)	S (cm^2)	GF	$G_i = \frac{I\ sample}{I\ ref.}$	$\eta_{opt} = \frac{G_i}{GF}$
2.5	6.25	0.73	0.46	0.63
5.0	25.0	1.45	0.53	0.366
7.5	56.25	2.18	0.717	0.329
10.0	100.0	2.91	0.783	0.269
15.0	225.0	4.36	0.94	0.216
20.0	400.0	5.81	0.93	0.160
25.0	750.0	7.27	1.2	0.165
30.0	900.0	8.72	1.38	0.158

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The general procedure as hereinbefore set forth was repeated, however, in place of glass microscope slides there were used commercially available square PMMA plates of dimensions 10 x 10 x 0.3 cm thickness, in which dyes were dispersed throughout the entire bulk obtained from Rohm and Haas. The commercial names of the dopes plates are:

a. GS 740 Green
b. GS 2151 Yellow chartreuse
c. GS 323 Orange
d. GS 520 Red
e. GS 2152 Magenta

The results for Magenta are set forth in Table VIII

TABLE VIII - COLORED COMMERCIAL PLATES HAVING DIMENSIONS 10 x 10 x 0.3 cm AND A GF OF 8.33 WITH AND WITHOUT FURTHER DYE COVERING

PMMA plate 10x10x0.3cm with dye	Dye film	Direct Radiation (South) Gi =I/Iref	n_{opt} =Gi/Gf	Indirect Radiation (South) Gi = I/Iref	n_{opt}=Gi/Gf	Direct Radiation through clear Glass Window (South) Gi=I/Iref	n_{opt}=Gi/GF	Radiation through Glass Window (North) Gi=I/Io	$n_{opt}=\frac{i}{GF}$	Radiation through Glass Window (South)(Rainy Day) Gi=I/Io	$n_{opt}=\frac{Gi}{GF}$
GS 2152		1.4	0.17	1.96	0.24	2.1	0.25	4.4	0.53	2.69	0.32
GS 2152	+ clear	1.7	0.20	2.1	0.25	2.14	0.26	4.8	0.58	2.67	0.32
GS 2152	+ fluorol	1.75	0.21	2.2	0.27	2.17	0.26	5.2	0.63	2.4	0.29

From Tables IV and VIII it can be seen that the addition of dyes according to the present invention to commercially available fluorescent plates results in increased plate efficiency.

It is to be recognized that the plate efficiencies measured and recorded herein are the result of preliminary laboratory tests and do not represent the actual efficiencies which can be obtained when the process of thin film coating is optimized for commercial production, e.g., by centrifuging and controlled heating.

Similarly a more effective optical coupling between the solar cells and the plate edges, e.g., through use of refractive index matching will also result in greater efficiencies.

An additional way of increasing the efficiencies of plates according to the present invention is envisioned as being achieved by optimal positioning the plates in conjunction to highly diffusing surfaces in a manner known per se in the art [see, e.g., G. Lifante et al Luminescent Solar Concentrators as Bifacial Captor Solar Cells, 8 (1983) 355-360].

Use of gallium arsenide cells instead of silicon cells also improves efficiency.

A model house having dimensions 60 x 60 x 60 cm was prepared with panels according to the present invention. The panels covering the roof, which is declined at 45°, are of size 10 x 10 cm and coated with BASF-241, BASF-339 and Clear on silica glass doped by CE(III). Total area of roof is 3600 cm^2.

Under illumination of 1000 watt/cm^2 such a house provides electricity of 15 watts which operates appliances in the model house and can be stored in a storage battery.

From the above experiments it can be extrapolated that panels of $1m^2$ will provide electricity of 40 watts which means that a roof covered by $25m^2$ of panels will provide 1 K watt electricity under illumination of $1000W/m^2$ solar illumination at peak irradiation.

It will be further evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative embodiments and examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof and it is, therefore, desired that the present embodiments be considered in all respects as illustrative and not restrictive, reference being made to the appended claims, rather than to the foregcing description, and all changes which come with the meaning and range of equivalency of the claims are therefore intended to be embraced therein.

CLAIMS

1. A solar concentrator plate doped with a dye selected from the group consisting of Orange-Red, Fluorol, oxazine-4-perchlorate, LDS 730, LDS 750, BASF 339 and combinations thereof with each other and with Clear or 3-phenyl-fluoranthene.

2. A solar concentrator plate as claimed in claim 1 wherein said dye is dispersed in a thin film of glass or plastic material covering said plate.

3. A solar concentrator plate as claimed in claim 1 or claim 2 and covered by a thin film of protecting glass.

4. A solar concentrator plate as claimed in claim 3 wherein said thin film of protecting glass is doped by Ce^{3+}.

5. A solar concentrator plate as claimed in claim 1 wherein said dye is incorporated in said plate.

6. A solar concentrator plate as claimed in any one of claims 1 to 5 with a combination selected from; (a) Orange-Red and Clear dyes; or (b) Orange-Red and Fluorol dyes; or (c) Orange-Red and oxazine-4-perchlorate dye; or (d) Orange-Red and LDS 730; or (e) Orange-Red and LDS 750; or with Orange-Red dye alone.

7. A solar concentrator plate as claimed in claim 1 wherein each of said dyes has absorption and emission spectra and Stokes Shift as set forth in

Table 11 herein.

8. A luminescent solar collector for high efficiency conversion of solar energy to electrical energy wherein solar energy is converted to fluorescent radiation at longer wave lengths at which photovoltaic cells have a better efficiency comprising a solar concentrator plate as claimed in claim 1, said plate being provided with a photovoltaic cell at least at one of its lateral edges, said photovoltaic cell having a high efficiency in the region of the spectrum of the respective fluorescent radiation.

9. The use of a dye selected from the group consisting of Orange-Red, Fluorol, oxazine-4-perchlorate, LDS 730, LDS 750, BASF 241, BASF 339 and combinations thereof with each other and with Clear or 3-phenyl-fluoranthene.

10. A method of converting solar energy to electrical energy which comprises the use of a plate as claimed in claim 1.

Fig.1

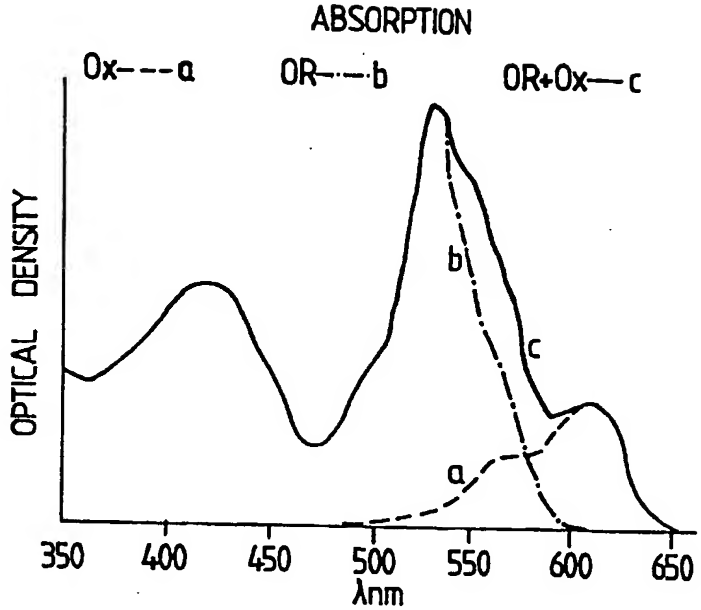

ABSORPTION
Ox---a
OR-·-b
OR+Ox—c
OPTICAL DENSITY
a
b
c
350
400
450
500
550
600
650
λnm

Fig.2.

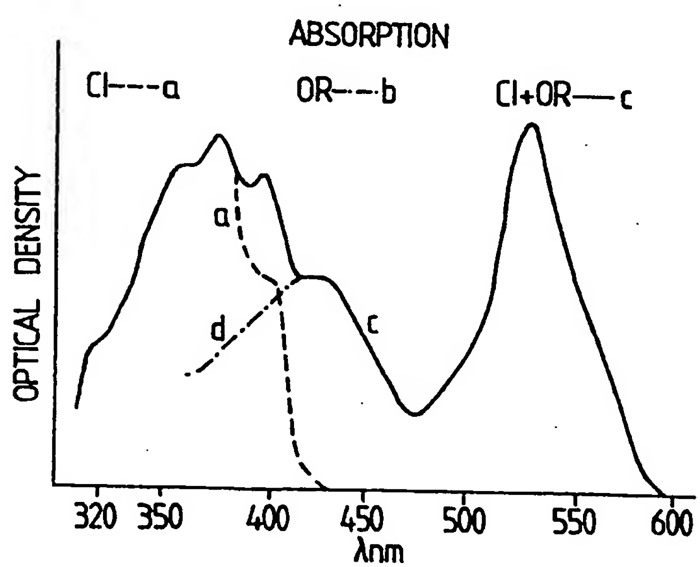

ABSORPTION
Cl---a
OR---b
Cl+OR—c
OPTICAL DENSITY
a
d
c
320
350
400
450
500
550
600
λnm

Fig.3.

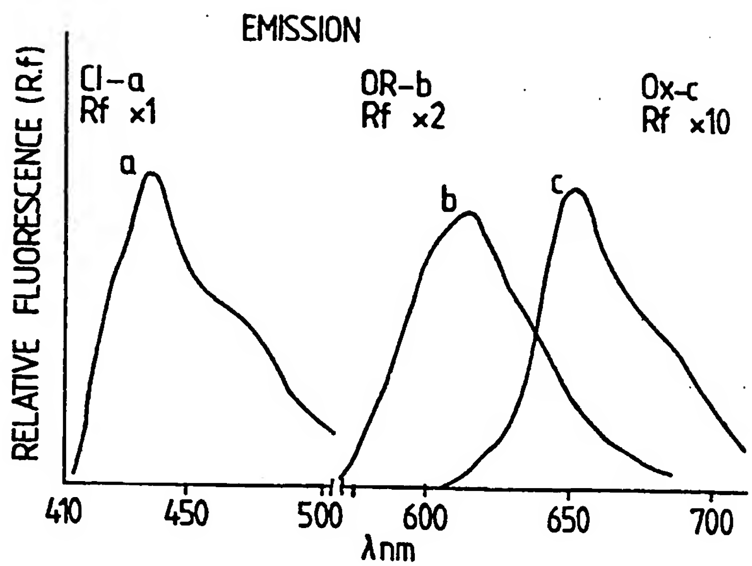

EMISSION
Cl–a
Rf ×1
OR–b
Rf ×2
Ox–c
Rf ×10
a
b
c
RELATIVE FLUORESCENCE (R.f)
410
450
500
600
650
700
λnm

Fig.4.

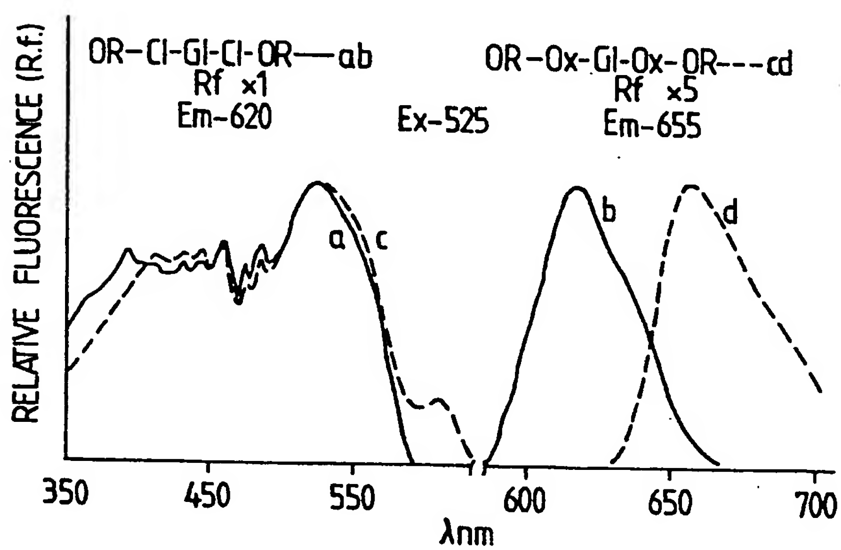

OR–Cl-Gl-Cl-OR—ab
Rf ×1
Em–620
Ex–525
OR–Ox-Gl-Ox-OR---cd
Rf ×5
Em–655
a
c
b
d
RELATIVE FLUORESCENCE (R.f.)
350
450
550
600
650
700
λnm

Fig.5.

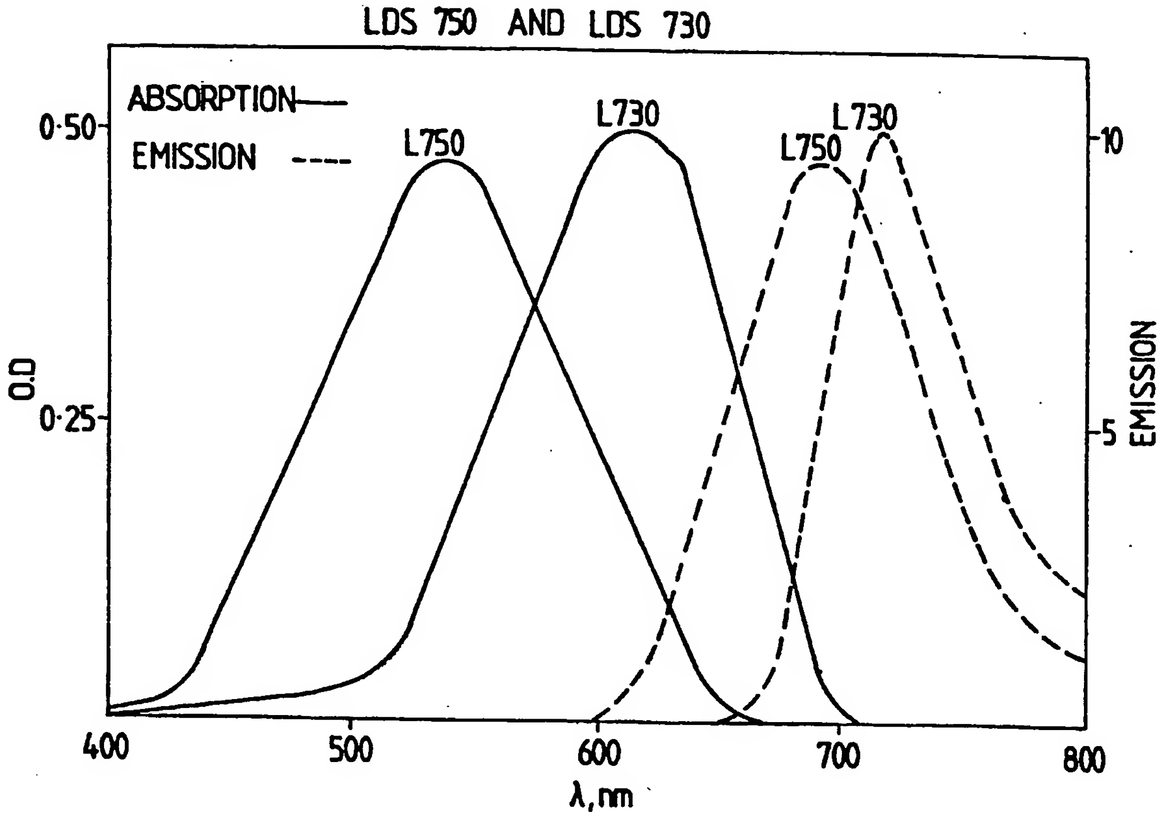
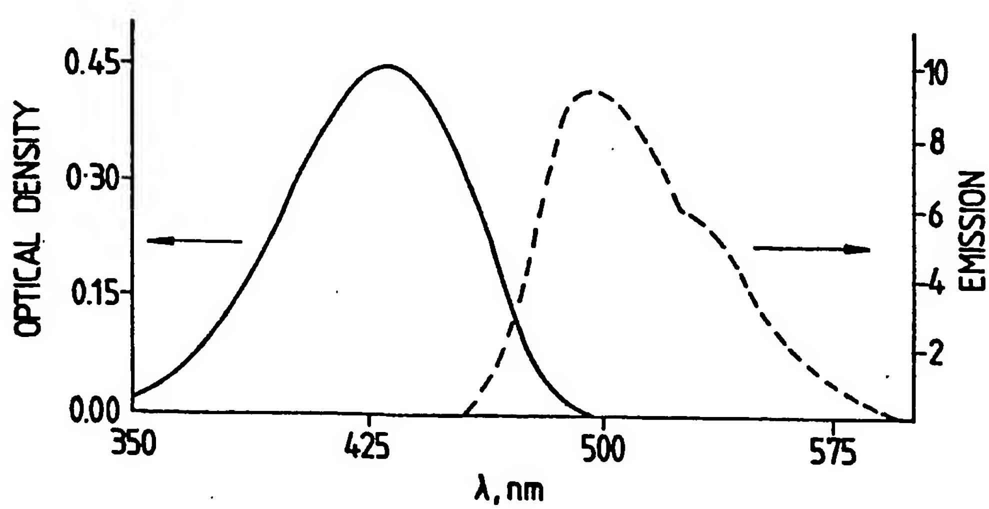
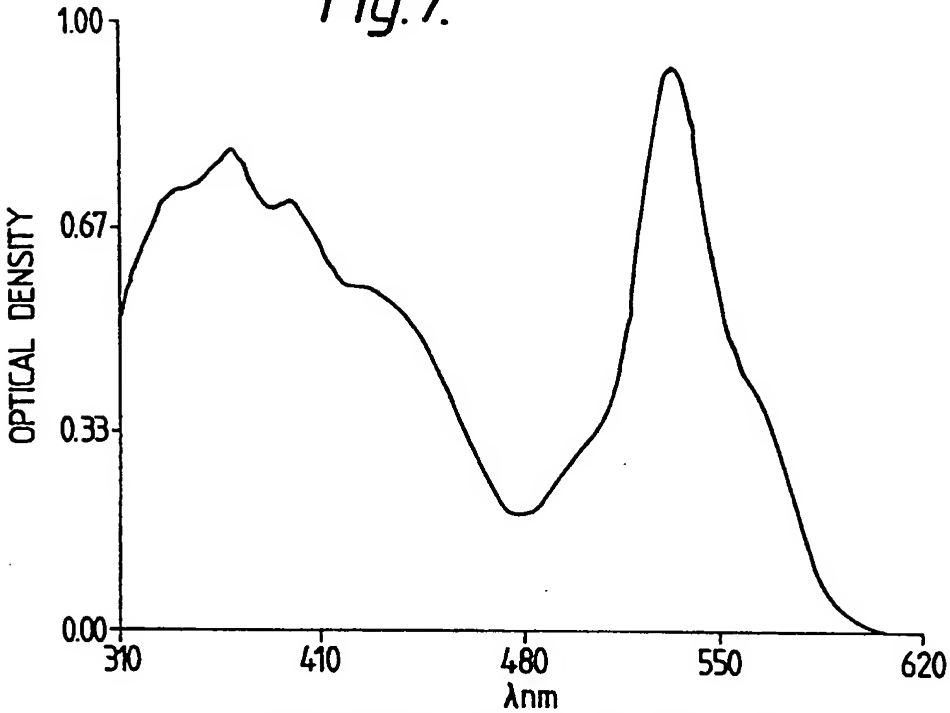


Fig.6.



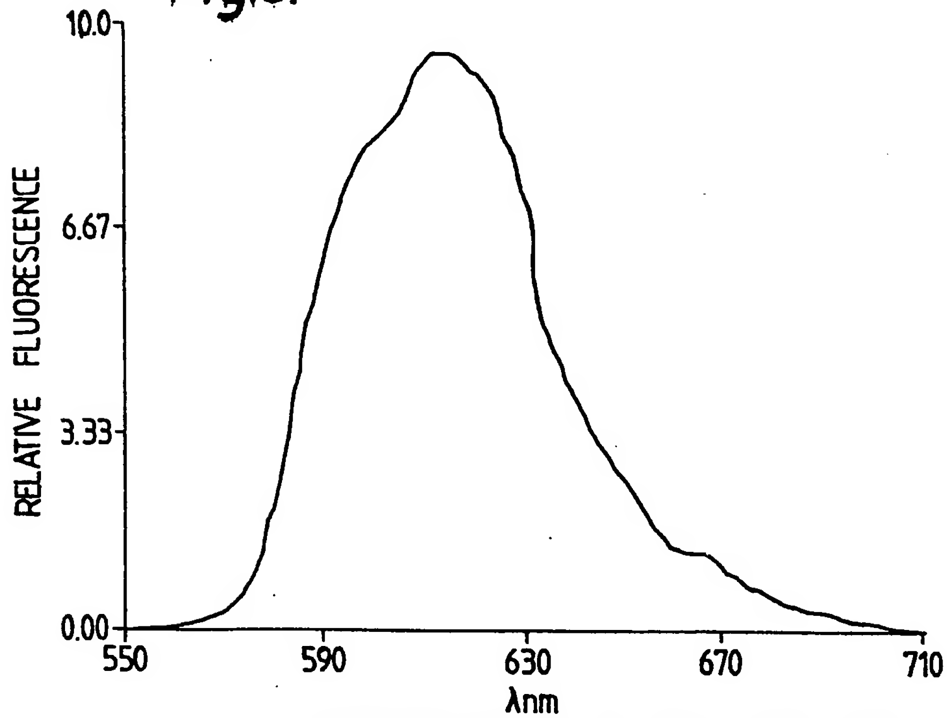
ABSORPTION AND EMISSION SPECTRA OF PMMA COATED BY FLUOROL-555

Fig. 7.



ABSORPTION SPECTRA OF PMMA COATED BY CLEAR, FLUOROL, ORANGE RED

Fig. 8.



EMISSION SPECTRA OF PMMA COATED BY CLEAR, FLUOROL, ORANGE RED

Fig.9

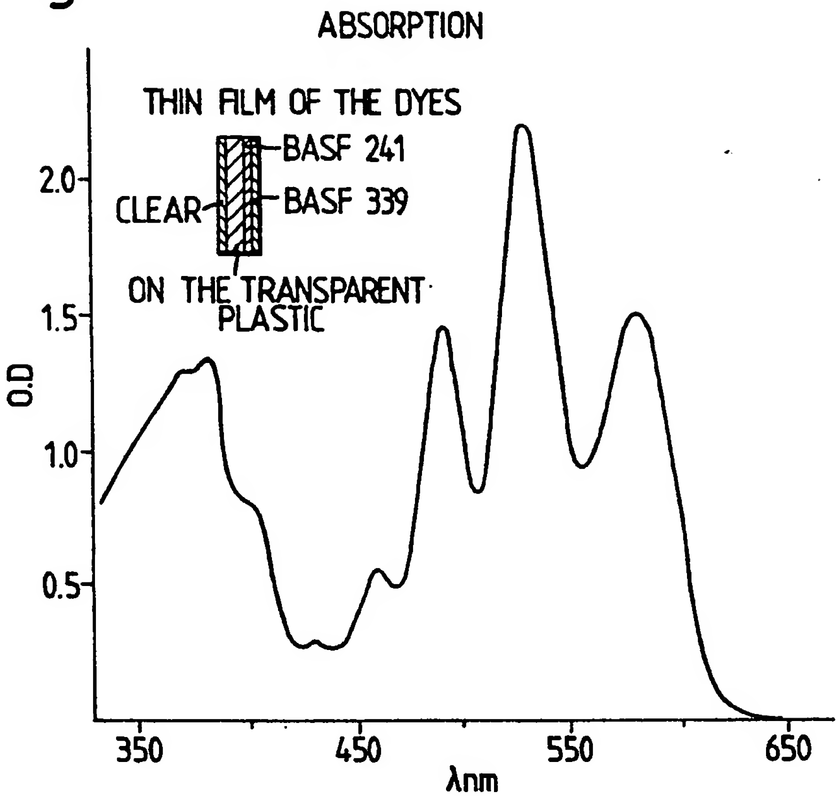
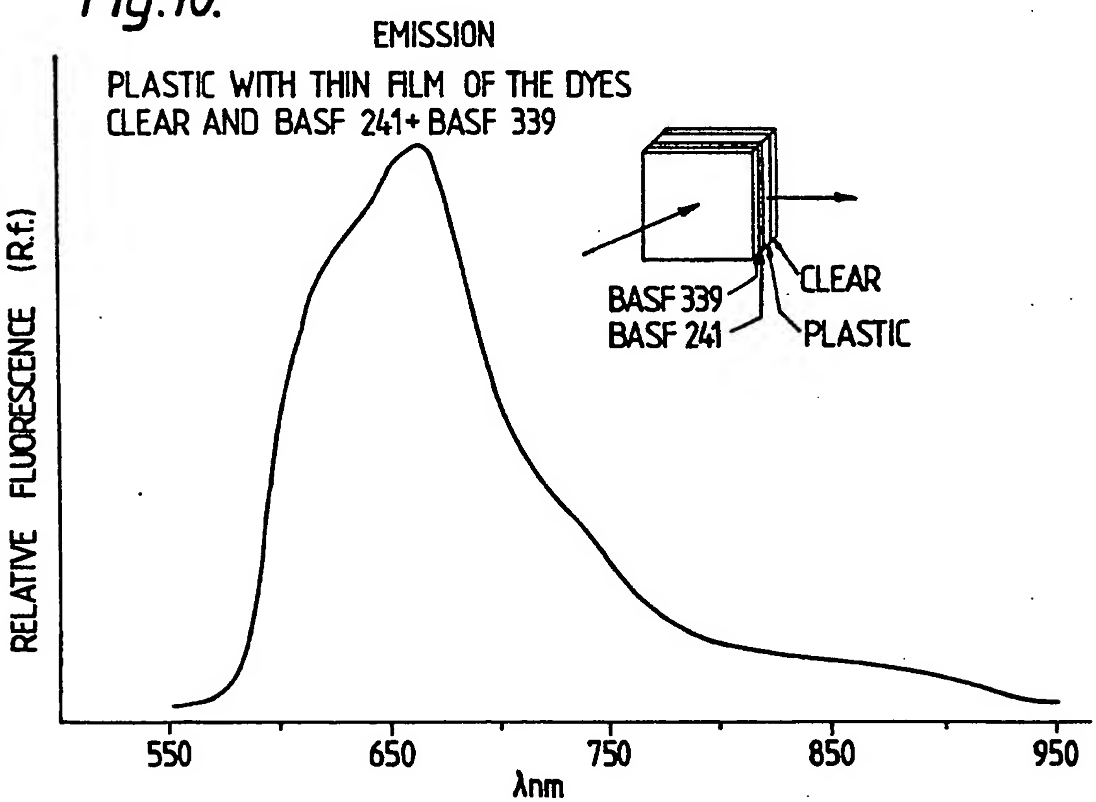

ABSORPTION
THIN FILM OF THE DYES
BASF 241
CLEAR
BASF 339
ON THE TRANSPARENT PLASTIC
O.D
2.0
1.5
1.0
0.5
350
450
550
650
λnm

Fig.10.


EMISSION
PLASTIC WITH THIN FILM OF THE DYES
CLEAR AND BASF 241+ BASF 339
CLEAR
BASF 339
BASF 241
PLASTIC
RELATIVE FLUORESCENCE (R.f.)
550
650
750
850
950
λnm